techcommentary

EPRI

Issues for Ozone for Drinking Water Treatment

Introduction

This *TechCommentary* examines recent developments in ozone technology for drinking water treatment in order to answer the following question: *Why should potable water plants consider the use of ozone at this time?*

Ozone in Drinking Water Treatment

The use of ozone to treat drinking water began in France in 1906. Today, approximately 3000 water treatment plants throughout the world use ozone, including an estimated 300 in the United States. In addition, nearly all suppliers of bottled water in North America ozonate their water as they are bottling it. Ozone-based treatment systems are being designed, installed, and operated at an increasing number of drinking water utilities across North America.

Applications of Ozone in Drinking Water Treatment

The most common ozone applications for drinking water treatment include:

- Primary disinfection of bacteria, viruses, and cyst organisms
- Reduction in concentration of unwanted disinfection by-products from chlorination
- Taste and odor control
- Coagulation assistance (microflocculation)
- Color destruction and removal
- Iron and manganese removal
- Destruction of sulfidic odors in groundwaters
- Solvent and pesticide destruction and removal.

However, primary disinfection and compliance with existing and planned EPA disinfection by-products regulations are the most current motivations for using ozone technologies in drinking water plants in the United States.

Because ozone is an unstable gas at normal temperatures, it cannot be bottled, transported, and stored. However, ozone can be generated safely at the water treatment site by using electrical energy, which is the main operating cost for ozone production. Although ozone costs in recent years have dropped significantly (see Figures 5 - 7 and Table II), its judicious application often leads to savings of other process chemicals. In such instances, ozone can be more cost-effective than seemingly cheaper water treatment approaches. Furthermore, ozonation results in aesthetically-pleasing finished water qualities.

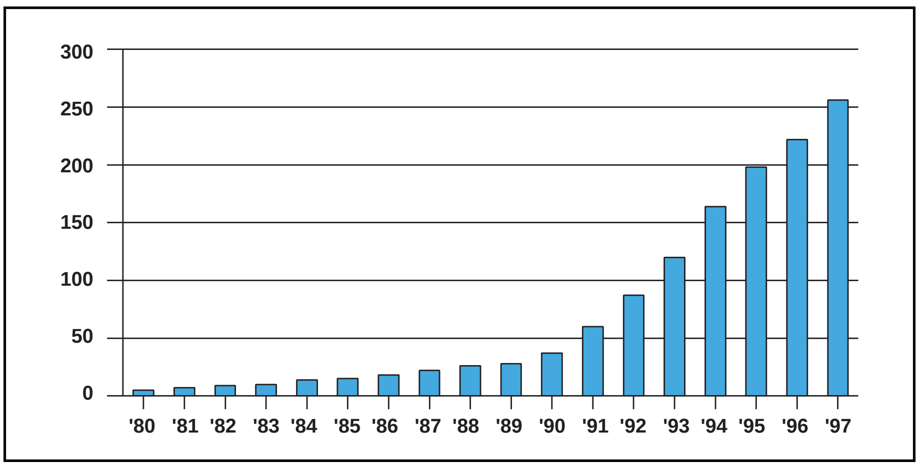

Figure 1. Growth of U.S. drinking water treatment plants using ozone. As of April 14, 1998, there were 264 plants (pictured) plus 363 residential and small businesses treating drinking water with ozone. (R.G. Rice)

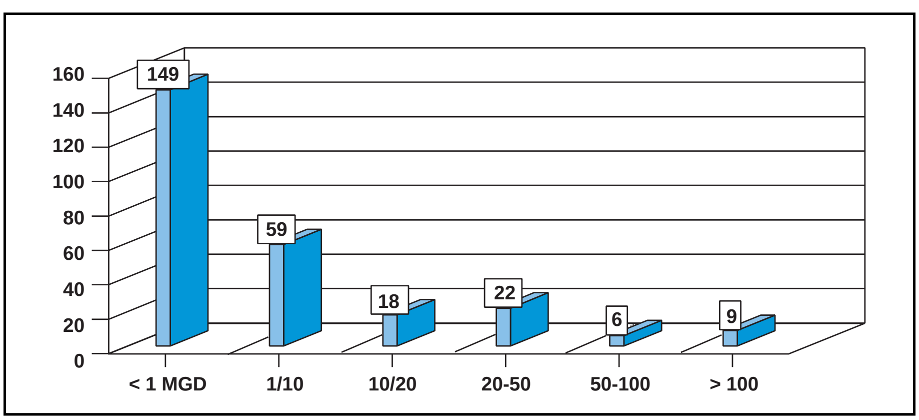

Figure 2. The 264 U.S. water plants using ozone, classified by MGD produced as of April 14, 1998. (R.G. Rice)

Growth of Ozone in U.S. Drinking Water Treatment Plants

The number of U.S. drinking water installations that use ozone has increased dramatically—from less than ten in 1980, to more than 100 in 1994, and to 264 in early 1998 (see Figure 1). Figure 2 shows these 264 operational plants grouped by production capacity. It is clear from these data that although ozone has a well-established place in treating water in medium and large-scale potable water plants, more than half of the known installations in the United States are small systems, defined by the U.S. EPA as plants which serve less than 10,000 persons.

Impacts of EPA Drinking Water Regulations on Ozone Acceptance

As is shown in Figure 1, appreciable growth in the number of potable water treatment plants using ozone began after the passage of the Safe Drinking Water Act Amendments of 1986. Those amendments led to the Surface Water Treatment Rule (SWTR), promulgated in 1991, which required the removal and/or inactivation of enteric viruses and *Giardia lamblia* cysts. These microorganisms were relatively new to the water industry. SWTR gave great impetus to the use of ozone as it is effective for disinfection.

While the virus and *Giardia* disinfection requirement could be met simply by increasing the level of chlorination, a Disinfectants/Disinfection By-products (D/DBP) rule was evolving simultaneously. This rule proposed to tighten restrictions on chlorinated organic by-products, causing the U.S. water industry to start looking seriously at the use of ozone.

Since the 1986 Amendments, new rules have been added and existing ones strengthened. Newer EPA regulations which encourage the use of ozone include the following:

- **Stage 1 of the D/DBP Rule** was published in December 1998. This rule reduces the current limits on trihalomethanes (THMs) that result from the addition of chlorine by 20% to 80 µg/L. It also establishes limits for a new class of disinfection by-products, haloacetic acids (HAAs), and bromate ions.
- **Stage 2 of the D/DBP Rule** is being negotiated and should be promulgated in May 2002. As proposed in 1994, the limits for THMs and HAAs are to be reduced by 50% from stage 1 levels.
- **Information Collection Rule** (the ICR) took effect in 1996. This rule required large water systems to collect data on the effectiveness of their water treatment processes. Over 525 U.S. water treatment plants were required to collect this information and submit it monthly to the EPA for 18 months. The information will be released by the EPA in stages, beginning in June 1999. It is expected that the water industry will have considerable information on the effectiveness of ozone to meet the current and future regulations.
- **Two Long-Term Enhanced Surface Water Treatment Rules** (the LT1ESWTR and the LT2ESWTR) will be promulgated by May 2002. Chemical inactivation of the more disinfectant-resistant cyst organism, *Cryptosporidium parvum*, is to be negotiated. Currently, only ozone and chlorine dioxide are proven to chemically inactivate *C. parvum* at levels which are practical in a water treatment plant, although UV radiation is showing promise for primary disinfection.

By-products from Ozonation

There are two types of by-products formed during ozonation—organic and inorganic. Although many organic by-products are produced from ozone oxidation of natural and synthetic organic materials, these are easily removed through biofiltration (oxygenated water passing through a filter bed of granular activated carbon).

On the other hand, bromate ion is a public health issue. Bromate ion is an inorganic oxidation product that can be produced when water containing bromide ion is ozonated. The toxicology of the bromate ion is still under study. Once defined, it may turn out that this material will not be of concern for humans. But that will not be determined for several years, and thus the EPA has set a maximum contaminant level (MCL) for bromate ion of 10 µg/L in Stage 1 of the D/DBP rule. Fortunately, when bromide ion is present in the source water at problematic concentrations, special process considerations for ozonation may be employed to minimize bromate ion production.

How Ozone is Generated

Ozone is a gas that is generated from oxygen by using electrical energy. Electrons split the oxygen molecules to form oxygen atoms that combine with other oxygen molecules to form ozone (O_3). Once produced, ozone's stability in air can be several hours but in water can range from a matter of seconds to tens of minutes, depending on a number of factors. For this reason, ozone cannot be stored like chlorine; rather, it must be generated on-site.

Inside an ozone generator, an electrical discharge gap is formed with a dielectric material (glass or ceramic) on one side and a ground electrode (stainless steel) on the other side (Figure 3). Either air or high-purity oxygen flows through the gap. High-voltage alternating current creates a flow of electrons across this gap. As the applied power increases, so does the flow of electrons, which, in turn, increases the ozone production rate. Since ozone generally is produced in concentrations of 1% to 15% by weight, then for every 100 lb (45.4 kg) of gas flowing through an ozone generator per

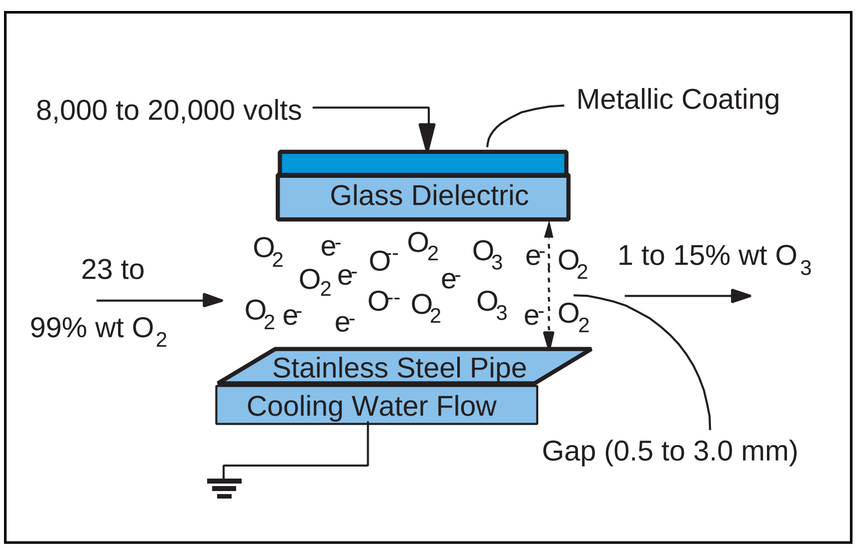

Figure 3. Section view of ozone generator dielectric. (K. Rackness)

hour, about 1 to 15 lb (0.45 to 6.75 kg) per hour of ozone is produced, depending on operating conditions. A flow of cooling water on the other side of the ground electrode is used to remove heat generated from the process.

Feed-gas options for ozone systems include air, high purity oxygen, or mixtures of air and oxygen. Air-feed systems require equipment to compress air and remove moisture and dust, such as compressors, dryers, and filters. Recently, liquid oxygen (LOX)-fed systems have become popular, due to the development of more-efficient generation equipment that is capable of producing higher concentrations. Some larger plants produce their own oxygen, while small to medium plants use either LOX or small oxygen concentrators, depending on their distance from a LOX supplier.

Ozone is introduced into the water by use of a contactor. Typical devices include bubble diffusers (the most common type), mechanical mixers, injectors, static mixers, submerged turbines, or packed column reactors.

Water Treatment Process Issues

Raw water quality impacts the manner by which ozone is used in a water treatment plant. For purposes of this discussion, there are four distinct types of raw water quality:

- "Dirty" surface waters
- "Clean" surface waters
- Groundwater
- Hard water which requires softening.

Treatment of "Dirty" Surface Waters

Surface waters classified as "dirty" are those which contain turbidity-causing particulates or high levels of natural organic matter, usually measured as Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC). A common treatment practice for these types of surface waters is to add a flocculating chemical, allow time for most of the particulates and some of the TOC or DOC to coagulate and flocculate, pass the water through a sedimentation basin, then filter the supernatant. This type of surface water treatment process is called "conventional treatment" in the water industry.

Prior to regulations limiting the concentrations of THMs, it was customary to add chlorine early in the process, usually as the raw water enters the treatment plant. Because untreated or partially treated water can contain appreciable amounts of organic matter, the early application of chlorine increases the potential of forming halogenated organic by-products, including THMs and HAAs, to concentrations exceeding regulations.

The use of ozone allows disinfection to be done early in the process without forming halogenated organic compounds. Ozone can be applied to the raw water and/or to the settled water. Chlorine addition can be reserved for the finished water where very little organic matter remains.

In treating "dirty" surface waters, ozone normally is applied between sedimentation and filtration (intermediate ozonation) or at the raw water stage ahead of flocculation (preozonation), and in some cases, at both positions (two-stage ozonation). When ozone is applied in two stages, it is customary to use smaller dosages at the raw water stage. Any small concentrations of iron and manganese present will be oxidized during preozonation and will precipitate in the coagulation/sedimentation tank. Points of ozone addition are shown in Figure 4.

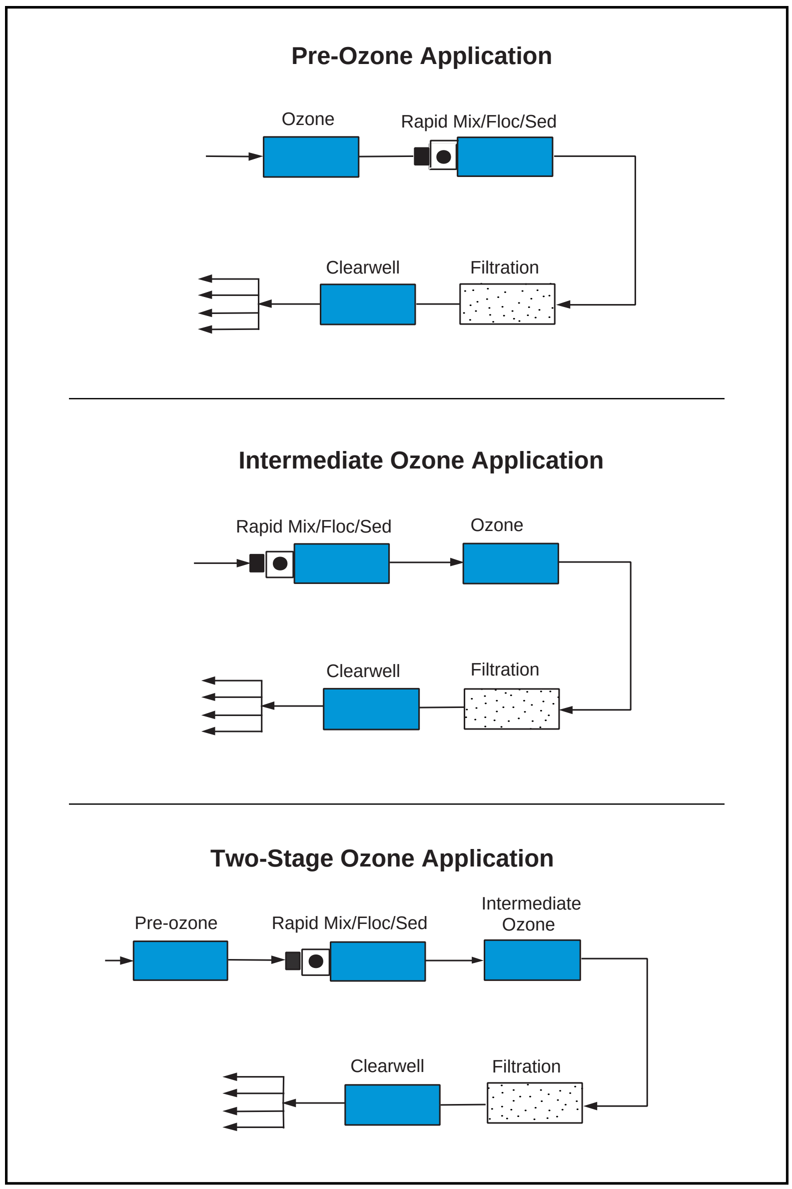

Figure 4. Three methods of applying ozone for drinking water treatment. (K. Rackness)

The dosage of ozone applied at the intermediate stage (after particulates and coagulated organics have been removed by sedimentation) can vary depending on its purpose. Lower doses can achieve primary disinfection. Higher doses are required for additional oxidation of dissolved organics, for color removal, for destruction of taste- and odor-causing organics, and to ensure primary disinfection of viruses, cysts, and bacteria.

In summary, the advantages of using ozone are

- It reacts with a large variety of organic compounds but produces no halogenated compounds
- It aids in the flocculation of particulate matter and enhances sedimentation
- It provides disinfection against more intractable microorganisms such as *Giardia* and *Cryptosporidium.*

The disadvantages of ozone are

- It is more expensive than chlorine
- It can form bromate ions if bromide ions are present

In addition, it is very reactive and thus does not provide a stable residual for use in distribution systems.

Treatment of "Clean" Surface Waters

"Clean" surface waters are those that contain significantly lower amounts of organic matter and turbidity, generally less than 5 NTU. Because of the low turbidity, coagulated water can be sent directly to the filters thus eliminating the sedimentation basins. This process is called direct filtration. With direct filtration, only preozonation can be utilized.

Treatment of Groundwater

When a strong oxidant, such as ozone, is added to groundwater that contains water-soluble forms of iron and manganese, the metal cations are rapidly oxidized and the resulting compounds then precipitate from the water and can be filtered. Because groundwater generally does not contain other particulates, the water at this point resembles "clean" surface water and thus the remaining treatment process is similar to a surface water direct filtration process. Other groundwater contaminants (such as sulfides, nitrites, and cyanides) are oxidized into less harmful compounds (sulfates, nitrates, cyanates, and carbon dioxide) during ozonation but remain water soluble, thus are not filtered. At the same time, bacteria and viruses will be inactivated when sufficient ozone and contact time are provided. There are cheaper alternatives to ozone for removing iron or manganese; however, ozone can be justified if other contaminants must be removed or disinfection must be achieved.

Advanced Oxidation with Ozone

Some groundwaters are contaminated with halogenated organics, such as trichloroethylene (TCE), perchloroethylene (PCE), or pesticides, which are hard to destroy by oxidation. These materials can be removed from groundwaters by adsorption onto granular activated carbon (GAC), but the process is costly and the chemicals still have to be destroyed later.

Ozone and other oxidants by themselves have little effect on TCE, PCE, or pesticides. Fortunately, combinations of ozone with UV_{254} radiation or ozone with hydrogen peroxide produce the stronger-than-O_3 species, hydroxyl free radical. In turn, the hydroxyl free radical is capable of destroying PCE, TCE, and other hard-to-oxidize organics by processes known as "advanced oxidation." Although not in widespread use, advanced oxidation is being employed at a few U.S. water treatment plants specifically to destroy these types of refractory organics.

Treatment of Hard Water by Softening

Hard waters are those which contain high levels of calcium and magnesium. The usual procedure for removing these substances is to elevate the pH of the water by adding lime, which converts bicarbonate anions present in the water into carbonate ions. The calcium and

Table I. Guidelines for Estimating Ozone Feed Locations and Dosage (K. Rackness)

Water Quality	Ozone Feed Locations	Typical Ozone Dosage	
		mg/L	lb/MG
Category I—Raw Turbidity < 10 NTU Ozone demand < 1 mg/L	Preozonation	2-4	16-34
Category II—Raw Turbidity >10 NTU Ozone demand < 1 mg/L	Intermediate Ozonation	2-4	16-34
Category III—Raw Turbidity <10 NTU Ozone demand > 1 mg/L	Pre- or Intermediate Ozonation	3-6	25-50
Category IV—Raw Turbidity >10 NTU Ozone demand > 1 mg/L	Intermediate or Two-Stage Ozonation	3-6	25-50

magnesium cations bond with the carbonate ions to form insoluble carbonates. The added lime also serves as a flocculating agent for some of the dissolved organics. After filtration, carbon dioxide or mineral acid is added to the water in order to restore the pH to its original, neutral level (approximately 7).

Application of ozone in a softening process is a bit tricky because of the elevated pH during some part of the treatment. If ozone is added at the high pH stage, it will immediately decompose to produce the hydroxyl free radical, which, although it is a much stronger oxidizing agent than molecular ozone (O_3), has only a microsecond half-life. This means that ozone added at the elevated pH will decompose without providing any treatment advantage. Thus care should be taken to add ozone at pH 9 or below in lime softening treatment processes.

Issues Related to Ozone Retrofits

When an ozone system is to be retrofitted into an existing water treatment plant, certain engineering issues must be addressed. These are the hydraulic profile, type and location of ozone contactor, and electrical system requirements. Typically the most desirable and cost-effective location for the ozone contactor is between the sedimentation tanks and the filters. However, this may necessitate repumping of the treated water to provide the necessary head (one to three feet on the average) to accommodate the headloss through a diffuser-type ozone contactor. As an alternative, sidestream ozone injection can be used that minimizes headloss, but it is not as energy-efficient.

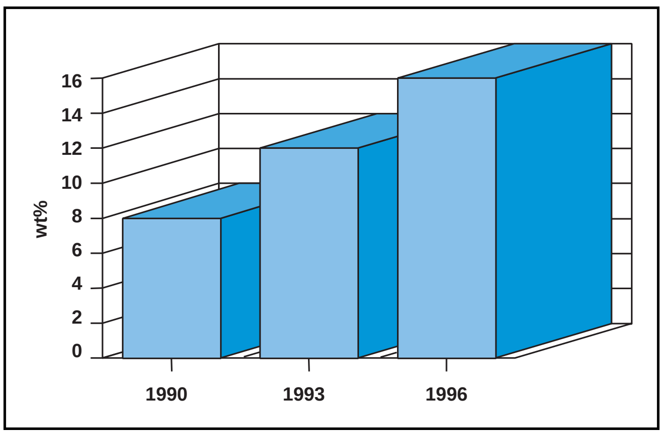

Figure 5. Increase in ozone concentrations in oxygen produced by new technologies. (Dyer-Smith, 1997)

With the addition of an ozone system, electric power demands will increase and the adequacy of the existing electrical service needs to be checked. Air preparation (if used), ozone generation, and some contacting require electric power. For a LOX-feed ozone system, the power demand is about 1.8 to 2.0 kW per MGD per mg/L of ozone; for an air-feed ozone system, about 3.5 to 4.0 kW per MGD per mg/L of ozone is required.

Process Considerations Summary

Table I provides guidelines for ozone dosages and feed locations for four different types of surface water sources. The first two categories have low ozone demand (< 1 mg/L) and a range of turbidities. The last two categories have high ozone demands (> 1 mg/L) and a range of turbidities. High turbidity often, but not necessarily, translates into high ozone demand. Column 2 shows the point(s) of expected ozone addition for these four types of raw waters, and Columns 3 and 4 show typical ozone dosages that each of these four types of water might require. The dosages shown are typical, but pilot studies are recommended before design of an ozone system.

Ozone System Costs

Energy usage for ozone may range from 100 to 400 kWh/MG (million gallons of water produced) or more, depending on raw water quality, finished water quality desired, treatment system design, and process operation. The associated electrical expense of producing ozone may

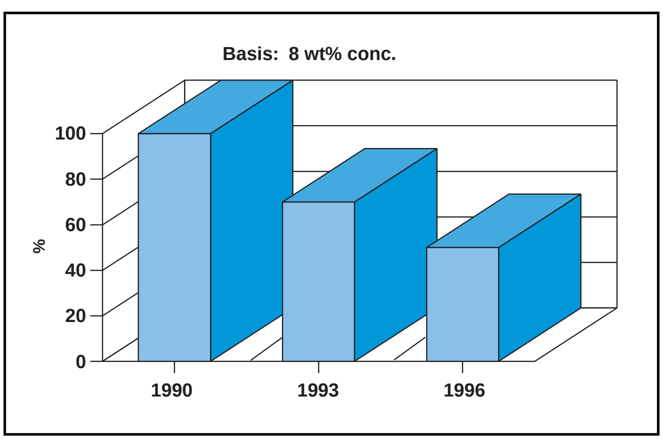

Figure 6. Evolution of ozone energy costs, 1990-1996. (Dyer-Smith, 1997)

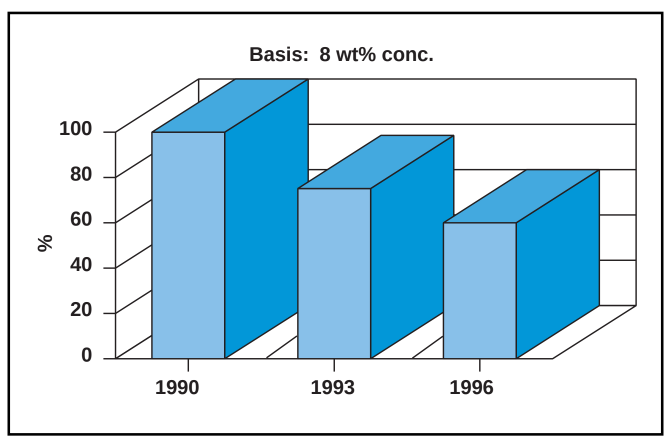

Figure 7. Evolution of ozone equipment costs, 1990-1996. (Dyer-Smith, 1997)

range from $10/MG to $40/MG or more, depending on local energy prices and ozone usage. Electrical energy and feed gas costs represent about 75% of the total cost of operating an ozone system.

Recent technological changes have lowered the cost of ozone treatment. Through the use of new ceramic dielectrics and electronic components in commercially available ozone generators, startling increases in ozone concentration (which improve ozone utilization) have been attained (see Figure 5). Because of these increases, the electrical energy costs to produce a given quantity of ozone and the cost of ozone equipment have dropped dramatically, as shown in Figures 6 and 7.

Cost Comparisons

The costs to produce ozone can be compared to other unit costs for chemicals commonly used in water treatment, as shown in Table II. The unit cost of ozone is a function of system efficiency and the price of electricity. A well-designed air-fed ozone system has an efficiency of about 10 kWh per pound of ozone generated. Assuming $0.10 per kWh, the resulting unit operating cost of ozone is $1.00/lb ($2.20/kg). However, if electricity is available at $0.05 per kWh, the cost of ozone is lowered to $0.50/lb ($1.10/kg). Purchased LOX for oxygen-fed systems has similar unit costs while on-site produced gaseous oxygen systems (GOX) may be 30 to 40% lower.

Case Study—Water Treatment Costs at Elizabethtown

The Elizabethtown Water Company (New Jersey, USA) operates two water treatment plants using the same surface water source. The older plant uses conventional treatment with multi-media filtration and chlorination. A new 40-MGD plant that went on line in October 1996 employs two-stage ozonation; biofiltration through granular activated carbon (GAC), sand, and garnet; and final chlorination.

A recent Ozone Optimization Study has lowered the budgeted ozonation costs to about $13.50 per million gallons ($13.50/MG). As a consequence, the total chemical costs at both plants now are approximately equal ($51/MG). The requirements of the EPA's proposed Stage 2 Disinfectants/Disinfection By-products regulations are being met at both treatment plants. However, the newer ozonation plant produces a superior quality water that is more aesthetically-pleasing to consumers.

Table II. Example of Chemical Unit Costs

Chemical	Unit Price $/lb	Typical Dose mg/L	Typical Dose lb/MG	Unit Cost $/MG
Ozone	0.50 - 1.00*	3	25	12.50 - 25*
Chlorine	0.20	4	33	7
Potassium Permanganate	1.20	4	33	40
Powdered Activated Carbon	0.35	5	42	15
Alum	0.15	25	208	31
Coagulant Aid	1.60	1	8	13
Polyphosphate	1.20	1	8	10

* Electrical cost @ $0.05 - $0.10/kWh and oxygen cost @ $50 - $70/ton ($0.06 - $0.08/kg)

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